

PATENT SPECIFICATION

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760,215

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COMPLETE SPECIFICATION

Manufacture of Alkanolamines

We, OXIRANE LIMITED, a British Company, of 170, Piccadilly, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of alkanolamines by the reaction of ammonia with ethylene oxide or 1,2-propylene oxide.

The reaction of aqueous ammonia with ethylene oxide to produce a mixture of mono-, di- and tri-ethanolamines is well known as is the analogous reaction between aqueous ammonia and 1,2-propylene oxide.

These reactions are discussed in Patent Specifications Nos. 642,950 and 655,580 which disclose the variations in the proportions of mono-, di- and tri-ethanolamines obtained with varying molar ratios of ammonia to ethylene oxide in the reaction mixture when aqueous ammonia of 0.92 density (about 22% aqueous ammonia) is reacted with ethylene oxide at 15° C. The processes of Patent Specifications Nos. 655,580 and 642,950 are concerned with the suppression of the formation of the monoalkanolamine and the dialkanolamine respectively.

Patent Specification No. 448,373 describes a process for the production primarily of monoalkanolamines by the reaction of ammonia with an alkylene oxide containing not more than 5 carbon atoms in the molecule, the reactants being present in the reaction mixture in the ratio of at least 20 mols. of ammonia per mol. of alkylene oxide. The specification states that the reaction is preferably carried out in the presence of water and in the liquid phase. Reaction temperatures are from 20° C. upwards, but it is stated that in the majority of cases it is preferred to operate in a temperature range of 90 to 150° C., pressures of from 30 to 250 pounds per square inch being quoted as suitable for the preferred temperature range when using a 20% ammonia solution. Patent Specification No. 448,373 also describes a continuous

method of operation and gives an example thereof in which isobutylene oxide is used. The reaction time for this example was 53 minutes and 73.2% of the isobutylene oxide employed was consumed.

Further United States Patent Specification No. 2,373,199 proposes the production of alkanolamines by the continuous reaction of ammonia with an alkylene oxide under substantially anhydrous conditions at a temperature between 120 and 275° C. We have found that the reaction of ammonia and ethylene oxide does not proceed to any appreciable extent in the absence of hydroxy bodies and that even with traces of water present at temperatures of 120° C. and above the reaction proceeds so slowly that it does not provide a satisfactory continuous process for use on an industrial scale. Apart from the limitations imposed by the size of the reactor prolonged reaction at high temperatures is liable to result in contamination and degradation of the products.

It is an object of the present invention to provide an improved continuous process for the production of alkanolamines by reaction of ammonia with ethylene oxide or 1,2-propylene oxide which can be operated with very short reaction times, i.e. reaction times of 30 minutes and under, with substantially complete reaction of the alkylene oxide introduced.

The process of the invention comprises continuously reacting ammonia with an alkylene oxide selected from ethylene oxide and 1,2-propylene oxide by continuously passing a liquid mixture of ammonia in aqueous solution, containing from 5 to 90% by weight of water, and the alkylene oxide, said mixture containing not more than 50% by weight of the alkylene oxide and from 1 to 45 molecules of ammonia for every three molecules of alkylene oxide present, through a reaction zone maintained at a temperature ranging from a minimum of 80 to 150° C. to a maximum of 275° C., under a pressure which ensures that the reaction mixture is

[F]

maintained in the liquid state throughout the reaction zone, the contact time within the reaction zone not exceeding 30 minutes and the amount of water and the temperature of the reaction zone being so adjusted in relation to each other that substantially complete reaction of the alkylene oxide takes place. Preferably the quantity of alkylene oxide present in the reaction mixture is not in excess of 35% by weight.

Heating is applied to the reaction zone to bring it to the minimum temperature of from 80 to 150° C., but when the reaction has been initiated it will generally be found necessary and it is indeed desirable to apply cooling to the reaction zone to remove heat evolved in the highly exothermic reaction which takes place and to ensure that the temperature of the reaction mixture does not rise above 275° C. The cooling should preferably be such as to ensure that after the initial rapid rise in temperature, the temperature in the reaction zone is rapidly reduced to close to 150° C. or below. The heating and cooling may be effected in the manner described below.

The contact time within the reaction zone required to ensure substantially complete reaction of the alkylene oxide depends primarily on the amount of water present and on the temperature of the reaction zone. The temperature may be adjusted by adjusting the minimum temperature to which the reaction zone is heated and it has been found to be a relatively simple matter in the process of the invention to keep the contact time below 30 minutes by elevating the minimum temperature or increasing the amount of water present within the limits specified. Thus the contact time may be kept below 30 minutes by elevating the minimum temperature to which the reaction zone is heated from 80 to 150° C. as the amount of water in the aqueous ammonia solution is decreased from 90% to 5%. In most cases it will be found possible by suitable choice of the water content of the aqueous ammonia and of the minimum temperature, to operate with contact times much shorter than 30 minutes. For example, in one form of the invention utilizing an aqueous ammonia containing from 10 to 35% by weight of ammonia in a reaction mixture containing not more than 35% by weight of alkylene oxide and heating the reaction zone to a minimum of 100° C., contact times of between 30 and 120 seconds may be employed. In another and the preferred form of the invention for the production mainly of monoalkanolamines, using a strong aqueous ammonia solution containing from 40 to 80% by weight of ammonia in a reaction mixture containing not more than 35% by weight of alkylene oxide, heating the reaction zone to a minimum temperature of 100 to 150° C. will enable a

contact time of 120 seconds or less to be used.

The minimum temperature to which the reaction zone is heated is preferably in the region of 100° C. when aqueous solutions of ammonia containing not more than 35% by weight of ammonia are used, and is preferably from 100 to 150° C. for stronger aqueous solutions of ammonia, temperatures of 120° C. and above being preferably used for aqueous solutions of ammonia containing about 80% or more by weight of ammonia.

The short contact times involved in the process of the invention enable one to use a compact, strongly constructed reactor in the form of a coil having a relatively high surface area to volume ratio which facilitates the rapid heating of the reaction mixture and also enables the heat of reaction to be removed rapidly from the reaction mixture. Both the heating and the removal of heat may satisfactorily be carried out by immersing the reactor in a bath of boiling liquid boiling at a temperature corresponding to the minimum temperature to which the reactants are heated, the vapour from the boiling liquid being passed to a condenser in which it is cooled and condensed and the condensed liquid being returned to the bath. By this means any excessive rise of the temperature within the reactor may be prevented and the reactants, after an initial and rapid rise in temperature may be rapidly cooled down to a temperature of 150° C. and below.

The amount of heat which is evolved in the process of the invention is limited by the stipulation that the alkylene oxide must not constitute more than 50% by weight of the material fed to the reactor. Thus, the maximum temperature to which the reactants will rise under adiabatic conditions can be calculated fairly accurately on the assumption that the specific heat of the reactants is 1 calorie per gm. per °C. and on the basis that the reaction of 1 gm. mol of ethylene oxide with ammonia evolves 26,000 cal. of heat. Thus, if a gms. of ethylene oxide are reacted with b gms. of ammonia in solution with c gms. of water, the temperature rise (adiabatic) is

$$\frac{a \times 26,000}{(a + b + c) \times 44} \text{ } ^\circ\text{C.}$$

As it is stipulated that a must not be greater than $b + c$, the maximum temperature rise is under 300° C. With propylene oxide, the maximum temperature rise is still smaller.

Using a coiled reactor formed of 75 ft. of stainless steel tube of 0.154" internal diameter and 0.25" external diameter immersed in a bath of boiling water, it has been found that on passing a reaction mixture of a 35% by weight aqueous solution of ammonia and ethylene oxide, containing 50% by weight of

ethylene oxide through the reactor, the temperature of the reaction mixture within the reactor may rise to approximately 200° C. but will then be rapidly reduced. The rise in temperature within the reaction zone due to the heat of reaction, is, providing it is not excessive or prolonged, not disadvantageous as it increases the rate of the reaction and also in the reaction with ethylene oxide, leads more rapidly to the decomposition of any quaternary ammonium hydroxide which may be formed. The effect of the latter is dealt with more fully below.

The invention has important advantages for the production of mono-alkanolamines in that by its means a crude product containing a relatively large proportion of alkanolamines of which the major part is monoalkanolamine, can be obtained.

Thus by reacting in accordance with the invention an aqueous ammonia containing 60% by weight of ammonia with ethylene oxide in the molecular ratio of ammonia to ethylene oxide of 7:1, using a reaction temperature of from 100–160° C., a pressure of 60 to 100 atmospheres and a contact time of 30 seconds, a crude product containing 23% by weight of ethanolamines, of which 60% by weight was mono-ethanolamine, was obtained.

On the other hand, despite the limitation on the proportion of alkylene oxide which may be present in the mixture of reactants in the process of the invention and the fact that the high temperatures employed enhance the formation of the monoalkanolamine, the process is flexible in that the molar ratios of ammonia to alkylene oxide may be varied within the wide limits to vary the amounts of mono-, di-, and tri- alkanolamines in the product of the reaction. Furthermore, in accordance with the invention, the product of the process described above may be reacted with a further quantity of alkylene oxide under similar conditions to those described above to increase the production of tri-alkanolamines. By the use of two or more stages in this manner the use of a large quantity of water which has subsequently to be evaporated may be avoided.

The manner in which the composition of the product of the process of the invention varies with the molar ratio of ammonia to ethylene oxide in the reaction mixture is illustrated by the curves shown in Fig. 1 of the accompanying drawings. These curves were obtained by carrying out a number of experiments in which a 25% by weight aqueous ammonia solution and ethylene oxide were reacted in varying molar ratios of ammonia to ethylene oxide in the reactor coil described above. The coil was immersed in a bath of boiling water and the temperature in the coil was within the range 100 to 200° C. In each case the product was freed of excess

ammonia and water and analysed. Curves 1, 2, 3, and 4 show respectively the percentages of monoethanolamine, diethanolamine, triethanolamine and glycol ethers of triethanolamine found in the product. Rather similar curves were obtained for the reaction of ammonia with propylene oxide. Further, it was found that the results do not vary appreciably with different strengths of the ammonia solution.

It can be seen from Fig. 1 that when monoethanolamine is the desired reaction product a molar ratio of ammonia to ethylene oxide above 4 to 1 is most suitable. It will further be seen from Fig. 1 that the increase in the percentage of monoethanolamine in the product for ratios higher than 15 to 1 is relatively small so that there is no disadvantage in not using higher ratios which increase the requirement for plant capacity and the amount of water to be removed subsequently. It has in fact been found advantageous to use molar ratios not in excess of 10 to 1. When operating with the higher molar ratios required for the production of mono-alkanolamines in accordance with the invention it is advantageous to use strong ammonia solutions since the amount of water to be subsequently removed is thus reduced. Aqueous ammonia solutions containing from 40 to 80% by weight of ammonia, i.e. from 20 to 60% by weight of water, may most advantageously be used for this purpose.

In the production of diethanolamine it is seen that molar ratios between 1 to 1 and 4 to 1 are most satisfactory but that the percentage of diethanolamine in the reaction product after removal of ammonia and water, does not rise above about 40% by weight. The yield of diethanolamine can be increased by recovering the monoethanolamine in the reaction product and reacting this monoethanolamine in aqueous solution with ethylene oxide under similar conditions to those used for the reaction of ammonia with ethylene oxide in accordance with the invention.

For the production of triethanolamine a molar ratio of ammonia to ethylene oxide of 1 to 3 is theoretically required. Thus to preserve the limitation, imposed because of thermal considerations, that the ethylene oxide shall not be more than 50% by weight of the reaction mixture it is necessary in a single stage process to use a very dilute solution of ammonia, in which case the increased amount of water will function as a thermal diluent. The production of triethanolamine as the major product may, therefore, be effected in a single stage using a very dilute aqueous ammonia solution, e.g. a 10% by weight solution. The production of triethanolamine may, on the other hand, be carried out in two stages, using a 35% by weight aqueous ammonia solution. In the two stage process the 35% ammonia solution may be reacted

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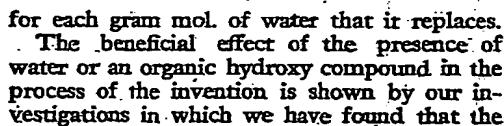
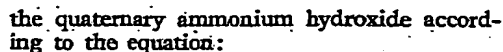
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The production of triethanolamine by the process of the invention takes place, with the formation of reduced amounts of the triethanolamine glycol ethers as by-products, compared with the amounts formed at lower temperatures. We have found that these ethers are formed by reaction between the triethanolamine present in the reaction mixture and ethylene oxide, according to the equation:



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rate of reaction of ethylene oxide with ammonia is directly proportional to the product of the molar concentration of ammonia,

the molar concentration of ethylene oxide, and the square of the concentration of hydroxy groups in gram equivalents per litre

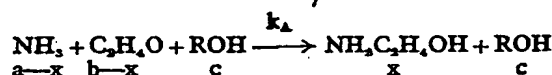
(i.e. total weight in grams of hydroxy groups per litre).

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present in the reaction system. This concentration of hydroxy groups is also given by the sum of the products obtained by multiplying the molar concentration by the number of hydroxy groups contained in the molecule for each hydroxy compound present.

In considering the reaction of ammonia with ethylene oxide when ammonia is present in considerable excess, e.g. 10 mols ammonia

to 1 mol. ethylene oxide, we find that if initially there are "a" mols/litre of ammonia, "b" mols/litre of ethylene oxide and "c" mols/litre of hydroxylic solvent ROH where "R" may be H, CH₃, etc. and, if after a time "t" seconds "x" mole/litre of ethylene oxide have reacted to give x mols of monoethanolamine, the reaction may be represented by the equation:



and that the reaction velocity may be expressed in the usual form:

$$\frac{dx}{dt} = k_A(a-x)(b-x)(c+x)^2$$

This equation assumes that the consequential reaction of monoethanolamine with ethylene oxide to form di-, and tri-ethanolamine is negligible in comparison with the reaction to produce monoethanolamine. This is so when "a" is large compared with "b." It can be seen from the equation for the reaction velocity that if ROH is absent, no reaction will take place.

Our measurements also show that the velocity constant of this reaction for 100° C., k_A has the value of $5 \times 10^{-4} \text{Ml}^{-1}\text{S}^{-1}$. Substitution of this value in the equation for the reaction velocity and integration of the resulting equation leads to the following times for the reaction which we have calculated for the reaction of 4 molar equivalents of ammonia with 1 of ethylene oxide, the ammonia containing varying proportions of water, the reaction being carried out at 100° C.:

	Concentration of ammonia in water % by weight	Times of reaction of ethylene oxide		
		10% secs.	50% secs.	95% secs.
55	30	2	11	55
	60	6	30	150
	80	9	144	720
	90	71	320	840
	95	261	940	1900
	98	1320	3150	4800
60	99	4000	6800	8300
	99.5	16000	22000	24000

It is seen that with a decrease in the amount of water, there is a slower initial reaction followed by a subsequently more rapid reaction. This is to be expected as mono-ethanolamine which is formed, is itself a hydroxylic body.

In practice we found that it was impossible to control the temperatures of the reaction of 35% and 60% ammonia to get any figures other than for complete reaction. In the case of 80% and higher strength ammonia, we were able to control the reaction temperature

at 100° C. and to obtain values for the times of reaction approximating to the calculated values given above. Even at 120° C. and higher temperatures we found no reaction between substantially anhydrous ethylene oxide and substantially anhydrous ammonia.

We have also found that there was a molar equivalence, in terms of the number of hydroxy groups contained in the molecule, between all hydroxylic solvents tested in their power to catalyse the reaction between ammonia and alkylene oxide.

Thus we have found that the presence in a unit volume of the reaction mixture of:

- 1 gram mol of water (18 grams)
 1 " " " " methanol (34 grams)
 5 1 " " " " phenol (94 grams)
 1/2 " " " " ethylene glycol (30.5 gms)
 or
 1/3 " " " " glycerol (30.7 grams)

has substantially the same effect on the reaction rate and time. The reaction velocity equation given above and the velocity constant cited, provide a method of calculating the reaction time and temperature, and thus of ensuring adequate control of the reaction and of avoiding the danger of explosion referred to by previous workers in this field.

One method of carrying out the process of the invention is described below with reference to Fig. 2 of the accompanying drawings, which illustrates diagrammatically a suitable apparatus for the carrying out of the invention.

Referring to Fig. 2 an aqueous ammonia solution of the desired strength, and the alkylene oxide, are separately and continuously pumped under pressure from storage vessels through supply lines 13 and 14 respectively, by means of proportionating pumps 11 and 12, to a mixing chamber 15 in which they are intimately mixed. The mixture of aqueous ammonia and alkylene oxide is then fed into a reactor coil 16. In the examples described below the coil used was a stainless steel coil 75 feet in length (when extended), with an external diameter of 0.25 inches and internal diameter of 0.154 inches. The reactor coil 16 is mounted in a vessel 17 and is completely immersed in vigorously boiling liquid 18, the vapour escaping from the surface of the liquid passing to a condenser 19, in which it is cooled and condensed, and then returned to the body of the liquid in the vessel 17. The liquid 18 is caused to boil vigorously by a heating fluid passing through a coil 21 in reboiler 20.

After passing through the reactor within the desired reaction time (which is governed by the pumping rate) the products are led through a needle let-down valve 22 which is adjusted to maintain the desired pressure within the reactor coil 16 and then into a distillation column 23, provided with a reboiler 24. Excess ammonia is distilled off in the column 23 and is led off by pipe 25. The aqueous alkanolamines are collected and pass through pipe 26 to storage or for further

treatment. The water may be removed from the aqueous alkanolamines by distillation, and the alkanolamines then separated from one another by fractional distillation under reduced pressure.

The invention may also be carried out as described above with part or all of the water of the aqueous ammonia solution replaced by a suitable organic hydroxylic solvent. The pressure applied to the reaction mixture must be such as will maintain the mixture in the liquid phase throughout the reaction zone. In view of the rise in temperature which takes place it is desirable to use a considerable excess of pressure and generally speaking pressures in excess of 60 atmospheres should be used.

The following examples, in all of which the procedure set out in the method of carrying out the invention described above with reference to Fig. 2 was used, illustrate the invention. In these examples the alkylene oxide was fully reacted, no free alkylene oxide being found in the reaction products.

EXAMPLES 1 TO 15.

In Examples 1 to 10 a mixture of an aqueous solution of ammonia and ethylene oxide was fed to the reactor. In Examples 11, 12 and 13 an aqueous solution of ammonia and propylene oxide was fed to the reactor.

Details of the Examples are set out in the following Table, in which:

Column A—gives the % by weight of ammonia in the aqueous solution of ammonia.	90
B—gives the molar ratio of ammonia to alkylene oxide in the mixture fed to the reactor.	95
C—gives the pressure applied to the system in atmospheres gauge pressure.	100
D—gives the temperature in °C. of the boiling liquid in which the reactor is immersed.	105
E—gives the contact time within the reactor in seconds.	110
F—gives the composition in percentages by weight of the alkanolamines in the product after the removal of excess ammonia and water. In Examples 1 to 10 the alkanolamines produced are the mono-, di-, and tri-ethanolamines and in Examples 11, 12 and 13 they are the mono-, di-, and tri-isopropanolamines.	

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TABLE

Ex. No.	(A)	(B)	(C)	(D)	(E)	(F)		
						Mono- alkanolamine	Di-	Tri-
1	25	7.5	70—90	100	300	68	24	8
2	25	4	70—90	100	300	49	38	13
3	25	1	70—100	100	38	18	24	58
4	10	0.4	70—100	100	282	3.3	12.6	79.2*
5	60	7	60—80	100	126	50	33	17
6	60	7	60—80	135	126	58	31	11
7	80	8.5	60—80	100	400	59	29	12
8	80	8.5	60—80	140	120	72	22	6
9	95	9	60—80	100	1200	60	31	9
10	95	9	60—80	149	92	69	25	6
11	25	10	60—80	100	45	74.5	24.5	1
12	25	1	60—80	100	60	20	44	36
13	60	2.5	60—80	100	180	37.5	50	12.5

* In example 4 the product after removal of excess ammonia and water also contained 4.9% of higher ethers.

EXAMPLE 14.

The ammoniacal aqueous product (i.e. the product containing unreacted ammonia and water) from Example 3 was cooled to 30° C. and continuously mixed with ethylene oxide in such proportions that the overall molar ratio of ammonia (i.e. reacted plus unreacted ammonia) to ethylene oxide (i.e. reacted plus fresh ethylene oxide) was brought to 1 to 2.5. This mixture was continuously passed through the reactor under the same reaction conditions as were used in Example 3.

The final product consisted of:

	% by weight
Ammonia	1.5
Water	28.3
Commercial triethanolamine	70.0

This "Commercial triethanolamine" was found on fractional distillation to contain:

	% by weight
Monoethanolamine	4.6
Diethanolamine	6.8
Triethanolamine	80.7
Higher Ethers	7.9

EXAMPLE 15.

The ammoniacal aqueous solution of isopropanolamines obtained as the product in Example 12 before distillation, was mixed in equal parts by volume with propylene oxide, bringing the overall molar ratio of propylene oxide to ammonia to 3.0 to 1.0, and the mixture passed through the reactor, which was surrounded by boiling water. A contact time of 90 seconds and an applied pressure of 60—80 atmospheres was used.

The resulting crude triisopropanolamine after removing excess ammonia and water had the following composition:

	% by weight
Monoisopropanolamine	Not found
Diisopropanolamine	3.0
Triisopropanolamine	93.1
Triisopropanolamine ether	3.9

EXAMPLE 16.

A solution of ammonia in methanol containing 60% by weight of ammonia was mixed with ethylene oxide to give a mixture in which the molar ratio of ammonia to ethylene oxide was 7:1, and this mixture was

passed through the reactor surrounded by a liquid boiling at 127° C. A pressure of 120—160 atmospheres was applied to the system and the contact time in the reactor was 120 seconds.

After removal of excess ammonia and methanol the resulting amines contained.

	% by weight
Monoethanolamine	63
Diethanolamine	30
Triethanolamine	7

EXAMPLE 17.

A solution of ammonia in water and methanol containing 60% by weight of ammonia, 20% by weight of methanol and 20% by weight of water was mixed with ethylene oxide to give a mixture in which the molar ratio of ammonia to ethylene oxide was 7:1. The mixture was passed through the reactor surrounded by a liquid boiling at 109° C. A pressure of 120 to 160 atmospheres was applied to the system and the contact time was 120 seconds.

The resulting amines, after removal of the water, methanol and excess ammonia, had a composition similar to that of the amines obtained in Example 1.

EXAMPLE 18.

A 50% solution by weight of ammonia in *n*-butanol was reacted with ethylene oxide in the reactor coil in a molar ratio of ammonia to ethylene oxide of 6.8:1. The reactor coil was immersed in a bath of liquid boiling at 127° C. and the pressure applied to the system was 120—160 atmospheres. A contact time of 132 seconds resulted in complete reaction of the ethylene oxide.

Excess ammonia and butanol were removed from the product and the resulting mixture of amines had a composition approximating closely to that of the amines obtained in Example 1.

EXAMPLE 19.

The monoethanolamine contained in the product of Example 2 above was recovered by fractional distillation under reduced pressure. 500 parts by volume of the recovered monoethanolamine, 125 parts by volume of water and 60 parts by volume of ethylene oxide were intimately mixed and the mixture fed to the reactor coil described above under a pressure of 40—60 atmospheres, the bath temperature being 100° C. The contact time within the reactor was 100 seconds. After removal of water and excess monoethanolamine the product had the following composition:

	% by weight
Diethanolamine	89
Triethanolamine	11

What we claim is:—

1. A process for the production of alkanolamines which comprises continuously reacting ammonia with an alkylene oxide selected from ethylene oxide and 1,2-propylene oxide by continuously passing a liquid mixture of ammonia in aqueous solution, containing from 5 to 90% by weight of water, and the alkylene oxide, which mixture contains not more than 50% by weight of the alkylene oxide and from 1 to 45 molecules of ammonia for every three molecules of alkylene oxide present, through a reaction zone maintained at a temperature ranging from a minimum of 80 to 150° C. to a maximum of 275° C., under a pressure which ensures that the reaction mixture is maintained in the liquid state throughout the reaction zone, the contact time within the reaction zone not exceeding 30 minutes and the amount of water in the said mixture and the temperature of the reaction zone being so adjusted in relation to each other that substantially complete reaction of the alkylene oxide takes place.

2. A process as claimed in claim 1, in which the said mixture contains not more than 35% by weight of alkylene oxide.

3. A modification of the process claimed in claim 1, or 2, in which part or all of the water in the reaction mixture is replaced by an equivalent amount, in terms of hydroxy group content, of an organic hydroxy compound containing only carbon, hydrogen and one or more alcoholic or phenolic hydroxy groups.

4. A process as claimed in claim 3 in which the said organic hydroxy compound is an alkyl alcohol boiling below 150° C.

5. A process as claimed in claim 2, in which the aqueous ammonia contains from 20 to 60% by weight of water and the reaction zone is maintained at a temperature ranging from a minimum of 100 to 150° C. to a maximum of 275° C.

6. A process as claimed in claim 2, in which the aqueous ammonia contains from 65 to 90% by weight of water and the reaction zone is maintained at a temperature ranging from a minimum of 100° C. to a maximum of 275° C.

7. A process as claimed in claim 5 or 6 in which the contact time does not exceed 120 seconds.

8. A process as claimed in claim 5, in which the said reaction mixture contains more than 4 and not more than 10 molecules of ammonia for each molecule of alkylene oxide present.

9. A process as claimed in claim 6 in which the said reaction mixture contains between 1 and 4 molecules of ammonia for each molecule of alkylene oxide present.

10. A process as claimed in claim 8 or 9, in which the alkylene oxide is ethylene oxide.

11. A process as claimed in any of the preceding claims in which said pressure is in excess of 60 atmospheres gauge pressure.

5 12. A process as claimed in claim 1 which comprises continuously passing a mixture of an aqueous ammonia, containing 60% by weight of ammonia, and ethylene oxide, said mixture containing 7 molecules of ammonia for each molecule of ethylene oxide
10 present, under a pressure of 60 to 100 atmospheres through a reaction zone maintained at a temperature of from 100 to 160° C., the contact time within the reaction zone being about 30 seconds.

15 13. A process as claimed in any of the preceding claims in which the reaction is carried out in a reactor in the form of a coil having a high surface area to volume ratio and immersed in a bath of boiling liquid
20 which serves initially to heat the reaction mixture to the required temperature and sub-

sequently to remove heat evolved during the reaction.

14. A process as claimed in any of the preceding claims followed by recovering the monoalkanolamine in the product and by
25 reacting said recovered monoalkanolamine with a further quantity of alkylene oxide in the presence of an hydroxy compound substantially as hereinbefore described.

15. A process for the production of alkanolamines substantially as hereinbefore described.

16. A process for the production of alkanolamines substantially as described in
35 any of examples 1 to 19.

17. Alkanolamines when produced by the process claimed in any of the preceding claims.

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6, Bream's Buildings, London, E.C.4,
Agents for the Applicants.

PROVISIONAL SPECIFICATION

Manufacture of Alkanolamines

40 We, OXIRANE LIMITED, a British Company, of 170, Piccadilly, London, W.1, do hereby declare this invention, to be described in the following statement:—

45 This invention relates to the manufacture of alkanolamines.

The reaction of aqueous ammonia with ethylene oxide to produce a mixture of monoethanolamine, diethanolamine, and triethanolamine, was described by Wurtz in
50 1860 (Liebig's Annalen der Chemie. Vol. 114 p. 51). This reaction, and the analogous one between aqueous ammonia and propylene oxide, has since then been widely described in the literature.

55 The reaction of ethylene or propylene oxide with aqueous solutions of ammonia is an exceedingly rapid one, and is accompanied by the evolution of approximately 26,000 cal. of heat per gram.mol. of ethylene or propylene oxide reacted. In view of the danger of explosion inherent in this process it has hitherto been the general practice in industry to carry out the reaction at temperatures between 0° and 50° C. and to add the
60 ethylene or propylene oxide slowly over a period of hours to the aqueous ammonia contained within a large reaction vessel, so that the amount of alkylene oxide present at any time in the reaction system is limited to a minimum.

70 More recently there have been references to the use of higher temperatures in the carrying out of such reactions. Thus Kedrinskii and K. H. Plaska in an article in Novosti Neftepereabatkii 1936.3 No. 4, 6 (which is summarised in Chemical Abstracts of the American
75 Chemical Society, Vol. 30, p. 6706, 1936)

described experiments in which ethylene oxide and ammonia were fed in stoichiometric quantities into a solvent medium at 60° C. The
80 resulting product consisted of 1.5% diethanolamine, 75% triethanolamine, 13% polymerised material and nearly 10% water. The yield based on ethylene oxide was only 89% of theory.

Further, Schwogler et al in U.S. patent No. 2,373,199 propose the production of alkanolamines by the continuous reaction of ammonia with an alkylene oxide under substantially anhydrous conditions at a temperature
90 between 120 and 275° C.

Our investigation of the reaction of ammonia and ethylene oxide has shown that the reaction does not proceed to any appreciable extent in the absence of hydroxy bodies. Further, we have found that even with traces of water present at temperatures of 120° C. and above, the reaction proceeds so slowly
95 that it does not provide a satisfactory continuous process for use on an industrial scale.

Apart from limitations imposed by the size of the reactor, prolonged reaction at high temperatures is liable to result in contamination and degradation of the products.

100 It is an object of the invention to provide a continuous process for the production of alkanolamines by the reaction of ammonia with ethylene oxide in which complete reaction of the ethylene oxide takes place within a relatively short time. It is further an object of the
105 invention to provide a process for the production of alkanolamines which is flexible in that it can be varied to produce mono-, di-, or triethanolamine as the main product.

115 In accordance with the present invention a

process for the production of alkanolamines consists in continuously reacting ammonia with an alkylene oxide having 2 or 3 carbon atoms in the molecule by continuously passing a mixture of the alkylene oxide, ammonia and water, containing not more than 50% by weight of alkylene oxide and containing more than 1% by weight of water, under a pressure which maintains the mixture in the liquid state through a reaction zone heated to at least 80° C. and maintained within the temperature range of 80 to 300° C., the contact time within the reaction zone being such that substantially complete reaction of the alkylene oxide takes place. It may be found necessary, and it is preferable, to apply cooling to the reaction zone to remove the heat of reaction and to ensure that the temperature of the reaction mixture does not rise above 300° C. and preferably does not rise above 275° C. The cooling may be applied in the manner described below.

The process of the invention may most suitably be carried out by reacting an aqueous ammonia containing from 2 to 95% and preferably from 5 to 90% by weight of water with the alkylene oxide. Furthermore the quantity of alkylene oxide in the reaction mixture is preferably not in excess of 35% by weight.

The contact time within the reaction zone depends primarily on the amount of water present and on the temperature to which the reaction zone is heated. Thus it has been found that using an aqueous ammonia containing 2% by weight of water and heating the reaction zone to 100° C., a contact time of about 2 hours is sufficient to ensure complete reaction of the ethylene oxide. Using the same temperature, the contact time may be decreased as the amount of water present is increased. Thus with 10% or more by weight of water and heating the reaction zone to 100° C. the contact time may be decreased to 30 minutes or less. Increasing the temperature to which the reaction zone is heated also results in a decrease of the contact time necessary to ensure complete reaction of the ethylene oxide.

Thus by suitable choice of the amount of water present in the reaction mixture and of the temperature, it is possible to operate the process of the invention with very short contact times. For example, in one preferred form of the invention utilising an aqueous ammonia containing from 10 to 35% by weight of ammonia in a reaction mixture containing not more than 35% by weight of alkylene oxide and heating the reaction zone to 100° C., the contact times of between 30 and 120 seconds may be employed. In another preferred form of the invention using a strong aqueous ammonia solution containing from 60 to 80% by weight of ammonia in a reaction mixture containing not more

than 35% by weight of alkylene oxide, heating the reaction zone to 120 to 140° C. will enable a contact time of 120 seconds or less to be used.

The temperature to which the reaction zone is initially heated is preferably in the region of 160° C. when aqueous solutions of ammonia containing not more than 35% of ammonia are used, and is preferably from 100 to 150° C. for stronger aqueous solutions of ammonia, temperatures of 120° C. and above being preferably used for aqueous solutions of ammonia containing about 80% or more by weight of ammonia.

As previously stated, it is generally necessary, and it is indeed preferable, to cool the reaction mixture to remove heat evolved in the highly exothermic reaction which takes place. Cooling is also preferable to ensure that after the initial, rapid rise in temperature within the reaction zone, the temperature is rapidly reduced to a point preferably below 150° C.

The short contact times involved in the process of the invention enable one to use a compact, strongly constructed reactor in the form of a coil having a relatively high surface to volume ratio which facilitates the rapid heating of the reaction mixture and also enables the heat of reaction to be removed rapidly from the reaction mixture. Both the heating and the removal of heat may satisfactorily be carried out by immersing the reactor in a bath of boiling liquid boiling at a temperature corresponding to the initial temperature to which the reactants are heated, the vapour from the boiling liquid being passed to a condenser in which it is cooled and condensed and the condensed liquid being returned to the bath. By this means any excessive rise of the temperature within the reactor may be prevented and the reactants, after an initial and rapid rise in temperature may be rapidly cooled down to a temperature of 150° C. and below.

The amount of heat which is evolved in the process of the invention is limited by the stipulation that the ethylene oxide must not constitute more than 50% by weight of the material fed to the reactor. Thus, the maximum temperature to which the reactants will rise under adiabatic conditions can be calculated fairly accurately on the assumption that the specific heat of the reactants is 1 calorie per gm. per °C. and on the basis that the reaction of 1 gm. mol of ethylene oxide with ammonia evolves 26000 cal. of heat. Thus, if *a* gms. of ethylene oxide are reacted with *b* gms. of ammonia in solution with *c* gms. of water, the temperature rise (adiabatic) is

$$\frac{a \times 26000}{a + b + c} \text{ } ^\circ\text{C.}$$

$$(a + b + c) \times 44$$

As it is stipulated that a must not be greater than $b + c$, the maximum temperature rise is under 300°C .

5 Using a coiled reactor formed of 75 ft. of stainless steel tube of 0.154" internal diameter and 0.25" external diameter immersed in a bath of boiling water, it has been found that on passing a reaction mixture of a 35% by weight aqueous solution of ammonia and ethylene oxide, containing 50% by weight of ethylene oxide through the reactor, the temperature of the reaction mixture within the reactor may rise to approximately 200°C . but will then rapidly be reduced.

15 The rise in temperature within the reaction zone due to the heat of reaction, is providing it is not excessive or prolonged, not disadvantageous as it increases the rate of the reaction and also in the reaction with ethylene oxide, leads more rapidly to the decomposition of any quaternary ammonium hydroxide which may be formed. The effect of the latter is dealt with more fully below.

25 Despite the limitation of the amount of ethylene oxide which may be used in the process of the invention and the fact that the high temperatures employed favour the formation of the monoalkanolamine, the process is flexible in that the molar ratios of ammonia to ethylene oxide may be varied within wide limits to vary the amounts of mono-, di-, and tri-alkanolamines in the product of the reaction. Furthermore, in accordance with the invention, the product of the process described above may be reacted with a further quantity of ethylene oxide under similar conditions to those described above to increase the production of triethanolamine. By the use of two or more stages in this manner the use of a large quantity of water which has subsequently to be evaporated may be avoided.

45 The manner in which the composition of the product of the process of the invention varies with the molar ratio of ammonia to ethylene oxide in the reaction mixture is illustrated by the curves shown on the accompanying drawing. These curves were obtained by carrying out a number of experiments in which a 25% by weight aqueous ammonia solution and ethylene oxide were reacted in varying molar ratios of ammonia to ethylene oxide in the reactor coil described above. The coil was immersed in a bath of boiling water and the temperature in the coil was within the range 100 to 200°C . In each case the product was freed of excess ammonia and water and analysed. Curves 1, 2, 3, and 4 show respectively the percentages of monoethanolamine, diethanolamine, triethanolamine and glycol ethers of triethanolamine found in the product. Rather similar curves were obtained for the reaction of ammonia with propylene oxide. Further, it was found

that the results do not vary appreciably with different strengths of the ammonia solution. 65

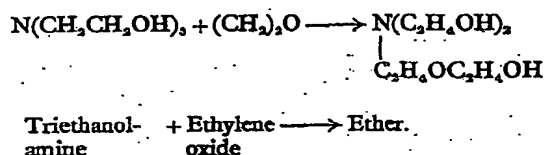
It can be seen from the accompanying drawing that when monoethanolamine is the desired reaction product a molar ratio of ammonia to ethylene oxide between 4 to 1 and 10 to 1 is most suitable. The increase in the percentage of monoethanolamine in the product for ratios higher than 10 to 1 is so small that it will not generally be found advantageous to use higher ratios. When operating at these molar ratios for the production of monoethanolamine or monoisopropanolamine as the major product it is an advantage to use strong ammonia solutions since the amount of water to be subsequently removed is reduced. 70 75 80

In the production of diethanolamine it is seen that molar ratios between 1 to 1 and 4 to 1 are most satisfactory but that the percentage of diethanolamine in the reaction product after removal of ammonia and water, does not rise above about 40% by weight. 85

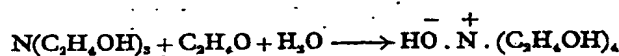
For the production of triethanolamine a molar ratio of ammonia to ethylene oxide of 1 to 3 is theoretically required. Thus to preserve the limitation, imposed because of thermal considerations, that the ethylene oxide shall not be more than 50% by weight of the reaction mixture it is necessary in a single stage process to use a very dilute solution of ammonia, in which case the increased amount of water will function as a thermal diluent. The production of triethanolamine as the major product may, therefore, be effected in a single stage using a very dilute aqueous ammonia solution, e.g. a 10% by weight solution. The production of triethanolamine may, on the other hand, be carried out in two stages, using a 35% by weight aqueous ammonia solution. In the two stage process the 35% ammonia solution may be reacted with ethylene oxide in the molar ratio of ammonia to ethylene oxide of 1 to 1, and the product so formed cooled to ambient temperatures and then reacted in a similar manner with further ethylene oxide. We have found that an overall ammonia to ethylene oxide molar ratio of 1 to 2.5 produces an optimum product in either method. The two stage process may be varied by removing the unreacted ammonia from the product of the first stage before reacting it with a further quantity of ethylene oxide. If this is done the molar ratio of ammonia (contained in the product) to ethylene oxide (contained in the product and added) is preferably 1 to 2.8. 90 95 100 105 110 115 120

The production of triethanolamine by the process of the invention takes place with the formation of reduced amounts of the triethanolamine glycol ethers as by-products, compared with the amounts formed at lower temperatures. We have found that these ethers are formed by reaction between the 125

triethanolamine present in the reaction mixture and ethylene oxide, according to the equation:



At relatively low temperatures triethanol- the quaternary ammonium hydroxide accord-
amine reacts with ethylene oxide to produce ing to the equation:



This hydroxide is a strong base and it is well known that alkalis catalyse the reaction of ethylene oxide with alcohols to form ethylene glycol ethers. It has been found that the rate of formation of these ethers is proportional to the amount of base present. At temperatures between 0° and 50° C. the quaternary ammonium hydroxide is stable but at higher temperatures and particularly above 100° C. this compound decomposes rapidly in the presence of water and ethanolamines to reform triethanolamine and ethylene oxide. Hence under the reaction conditions employed in the present process the concentration of the tetraethanol-ammonium hydroxide is reduced to a small value and hence the formation of the by-product ether is also reduced to a correspondingly small value.

Following on the above observations it has also been found that the addition of small amounts of acidic materials to the reaction mixture reduces the amounts of by-product ethers formed by neutralising any of the quaternary ammonium hydroxide present in the reaction mixture at the elevated temperatures employed. Examples of such acidic materials which may be added include boric acid, carbon dioxide, phosphoric acid and sulphuric acid.

The tri-isopropanolamine does not appear to form a quaternary ammonium hydroxide by reaction with propylene oxide, due no doubt to the steric factors involved, so that at all temperatures between 0° and 270° C. the reaction product is contaminated only with the tri-isopropanolamine glycol ethers, formed by the uncatalysed reaction between the tri-isopropanolamine and propylene oxide. Even though the uncatalysed formation of these ethers is slightly greater in the present process than the amounts formed in previous processes employing lower temperatures, it is still very advantageous to carry out the reaction in the manner described from the point of view of safety and economy of operation.

The present invention also includes a modification of the process of the invention set out above, in which the water in the reaction mixture is wholly or partially replaced by an organic hydroxy compound. Organic hydroxy compounds which may be used in this modification are the mono-, di-, and tri-alkanolamines produced by the process or other hydroxy compounds which contain no groups, other than an hydroxy group, which are reactive to ethylene oxide and which have a boiling point sufficiently distinct from that of the products to enable separation to take place without difficulty. Thus low boiling alcohols having a boiling point not above 150° C. and preferably not above 125° C., e.g. methanol and ethanol, may be used.

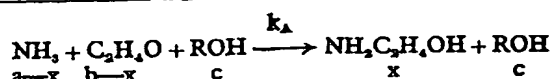
The amount of organic hydroxy compound present should be $\frac{1 \text{ gram mole}}{\text{Number of hydroxy groups}}$

for each gram mole of water that it replaces.

The beneficial effect of the presence of water or an organic hydroxy compound in the process of the invention is shown by our investigations in which we have found that the rate of reaction of ethylene oxide with ammonia is directly proportional to the product of the molar concentration of ammonia, the molar concentration of ethylene oxide, and the square of the molar concentration of hydroxide groups present in the reaction system. In considering the reaction of ammonia with ethylene oxide when ammonia is present in considerable excess e.g. 10 mols ammonia to 1 mol. ethylene oxide, we find that if initially there are "a" mols/litre of ammonia, "b" mols/litre of ethylene oxide and "c" mols/litre of hydroxylic solvent ROH where "R" may be H, CH₃, etc. and if after a time "t" seconds "x" moles/litre of ethylene oxide have reacted to give x moles of monoethanolamine, the reaction may be represented by the equation:

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and that the reaction velocity may be expressed in the usual form:

$$dx/dt = k_A(a-x)(b-x)(c-x)^2$$

- 5 This equation assumes that the consequential reaction of monoethanolamine with ethylene oxide to form di-, and tri-ethanolamine is negligible in comparison with the reaction to produce monoethanolamine. This is so when
10 "a" is large compared with "b." It can be seen from the equation for the reaction velocity that if ROH is absent, no reaction will take place.

Our measurements also show that the velocity constant of this reaction for 100° C.,
15 k_A has the value of $5 \times 10^{-4} \text{M}^{-1}\text{S}^{-1}$. Substitution of this value in the equation for the reaction velocity and integration of the resulting equation leads to the following times for the reaction which we have calculated for the
20 reaction of 4 molar equivalents of ammonia with 1 of ethylene oxide, the ammonia containing varying proportions of water, the reaction being carried out at 100° C.

25	Concentration of ammonia in water % by weight	Times of reaction of ethylene oxide.		
		10% secs.	50% secs.	95% secs.
30	30	2	11	55
	60	6	30	150
	80	9	144	720
	90	71	320	840
	95	261	940	1900
	98	1320	3150	4800
	99	4000	6800	8300
35	99.5	16000	22000	24000

It is seen that with a decrease in the amount of water, there is a slower initial reaction followed by a subsequently more rapid reaction. This is to be expected as monoethanolamine which is formed, is itself a hydroxylic body.

40 In practice we found that it was impossible to control the temperatures of the reaction of 35% and 60% ammonia to get any figures other than for complete reaction. In the case of 80% and higher strength ammonia, we were able to control the reaction temperature at 100° C. and to obtain values for the times of reaction approximating to the calculated values given above. Even at 120° C. and higher temperatures we found no reaction between substantially anhydrous ethylene oxide and substantially anhydrous ammonia.

55 We have also found that there was a molar equivalence between all hydroxylic solvents tested in their power to catalyse the reaction between ammonia and ethylene oxide.

Thus we have found that:

- 60 1 molar equivalent of water (18 grams)
1 " " " methanol (34 grams)
1 " " " phenol (94 grams)
1/2 " " " ethylene glycol (30.5 grams)
1 " " " monoethanolamine (61 grams)
65 1/3 " " " triethanolamine (49.7 grams)

have an equivalent effect on the reaction rates and time. The reaction velocity equation given above and the velocity constant cited, provide a method of calculating the reaction time and temperature, and thus of ensuring adequate control of the reaction and of avoiding the danger of explosion referred to by previous workers in this field.

70 In a preferred method of carrying out the invention an aqueous ammonia solution of the desired strength, and the alkylene oxide, are separately and continuously pumped under pressure from storage vessels, by means of proportionating pumps, to a mixing chamber in which they are intimately mixed. The mixture of aqueous ammonia and alkylene oxide is then fed into a reactor which consists of a coiled tube. In the examples described below the coil used was a stainless steel coil 75 feet in length (when extended), with an external diameter of 0.25 inches and internal diameter of 0.154 inches. The reactor is completely immersed in a bath of boiling liquid, the vapour escaping from the surface of the liquid passing to a condenser, in which it is cooled and condensed, and then returned to the body of the liquid in the bath.

75 After passing through the reactor within the desired reaction time (which is governed by the pumping rate) the products are led through an after cooler and thence through a needle let-down valve which is adjusted to maintain the desired pressure within the reactor. The
100

cooled, crude products may then either be further cooled and passed to a crude product reservoir, the product from which is removed and separately distilled to remove water and unreacted ammonia, or the crude products may be passed directly to a continuous stripping still to effect this separation. In either case the unreacted ammonia may be recycled for further use. The alkanolamines may then be separated from one another by fractional distillation under reduced pressure.

The invention may also be carried out as described above with part or all of the water of the aqueous ammonia solution replaced by a suitable organic hydroxylic solvent. The pressure applied to the reaction mixture must be such as will maintain the mixture in liquid phase throughout the reaction zone. In view of the rise in temperature which takes place it is desirable to use a considerable excess of pressure and generally speaking pressures in excess of 60 atms. should be used.

The following examples, in all of which the procedure set out in the preferred method of carrying out the invention described above was used, illustrate the invention. In these examples the alkylene oxide was, except where otherwise stated, fully reacted, no free alkylene oxide being found in the reaction products.

EXAMPLE 1.

A 25% by weight aqueous solution of ammonia, and ethylene oxide, were continuously mixed in the ratio of 1000 ml. of ammonia solution (containing 13 mols. of ammonia) with 86.5 ml. of ethylene oxide (1.73 mols.) so that the molar ratio of ammonia to ethylene oxide was 7.5 to 1. This mixture was continuously fed to the reactor coil which was immersed in a bath of boiling water. A pressure of 70 to 90 atms. gauge was applied to the system and the pumping rate was adjusted to give a contact time within the reactor of 5 minutes.

After removal of unreacted ammonia and water by distillation the reaction product was found to contain:

	% by weight
Monoethanolamine	68
Diethanolamine	24
Triethanolamine	8

EXAMPLE 2.

Example 1 was repeated with a mixture of a 35% by weight aqueous solution of ammonia and ethylene oxide, in which the molar ratio of ammonia to ethylene oxide was 25 to 1.

The resulting product, after removal of excess ammonia and water, had the following composition:

% by weight

Monoethanolamine	78
Diethanolamine	16
Triethanolamine	6

EXAMPLE 3.

Reaction of a mixture of a 25% by weight aqueous ammonia solution with ethylene oxide in a molar ratio of ammonia to ethylene oxide of 4 to 1, under the same temperature, pressure and contact time conditions as in Example 1, resulted in the following composition of the product, after removal of unreacted ammonia and water:

% by weight

Monoethanolamine	49
Diethanolamine	38
Triethanolamine	13

EXAMPLE 4.

A mixture of equimolecular quantities of ammonia (present as a 25% by weight solution in water) and ethylene oxide were passed under a pressure between 70 and 100 atmospheres through the reactor, the residence time therein being 38 seconds, and the reactor being surrounded by a bath of boiling water. The reaction product, after removal of unreacted ammonia and water consisted of:

% by weight

Monoethanolamine	18
Diethanolamine	24
Triethanolamine	58

No tetraethanolammonium hydroxide or higher ethers were found to be present.

EXAMPLE 5.

The ammoniacal aqueous product (i.e. the product containing unreacted ammonia and water) from Example 4 was cooled to 30° C. and continuously mixed with ethylene oxide in such proportions that the overall molar ratio of ammonia (i.e. reacted plus fresh ethylene oxide) was brought to 1 to 2.5. This mixture was continuously passed through the reactor under the same reaction conditions as were used in Example 4.

The final product consisted of:

% by weight

Ammonia	1.5
Water	28.3
Commercial triethanolamine	70.0

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This "Commercial triethanolamine" was found on fractional distillation to contain:

	% by weight
5 Monoethanolamine	4.6
Diethanolamine	6.8
Triethanolamine	80.7
Higher Ethers	7.9

EXAMPLE 6.

10 A mixture of a 10% by weight aqueous solution of ammonia and ethylene oxide, in which the molar ratio of ammonia to ethylene oxide was 1 to 2.5, was continuously passed through the reactor, which was surrounded by boiling water. The residence time within the reactor was 4.7 minutes and a pressure of between 70 and 100 atmospheres was applied to the system.

20 The product was discharged into a continuous stripping still which removed unreacted ammonia and water. On fractional distillation the product was found to have the following composition:

	% by weight
25 Monoethanolamine	3.3
Diethanolamine	12.6
Triethanolamine	79.2
Higher Ethers	4.9

EXAMPLE 7.

30 A 25% by weight aqueous solution of ammonia and propylene oxide were continuously mixed in such proportions that the molar ratio of ammonia to propylene oxide in the mixture was 10 to 1. The mixture was continuously passed through the stainless steel reaction coil which was surrounded by boiling water, the residence time in the coil being 45 secs. A pressure of 60—80 atmospheres was applied to the system in order to keep the reactant in the liquid phase.

40 The emerging liquid was distilled to remove excess ammonia and water. The resulting mixture of isopropanolamines was found to have the following composition:

	% by weight
45 Monoisopropanolamine	74.5
Diisopropanolamine	24.5
Triisopropanolamine	1.0

EXAMPLE 8.

50 Ammonia (in the form of a 25% by weight aqueous solution in water) and propylene oxide were mixed in equimolecular proportions and the mixture passed under a pressure of 60—80 atmospheres through the reactor surrounded by boiling water, the residence time in the reactor being 60 seconds. The resulting product was distilled to remove excess ammonia and water and the resulting mixture of isopropanolamines had the following composition:

% by weight

Monoisopropanolamine	20	60
Diisopropanolamine	44	
Triisopropanolamine	36	

EXAMPLE 9.

The ammoniacal aqueous solution of isopropanolamines obtained as the product in Example 8 before distillation, was mixed in equal parts by volume with propylene oxide, bringing the overall molar ratio of propylene oxide to ammonia to 3.0 to 1.0, and the mixture passed through the reactor, which was surrounded by boiling water. A contact time of 90 secs. and an applied pressure of 60—80 atmospheres was used.

75 The resulting crude triisopropanolamine after removing excess ammonia and water had the following composition:

% by weight

Monoisopropanolamine	not found	
Diisopropanolamine	3.0	
Triisopropanolamine	93.1	80
Triisopropanolamine ether	3.9	

EXAMPLE 10.

85 A mixture of a 60% by weight aqueous solution of ammonia and propylene oxide in the molar ratio of ammonia to propylene oxide of 2.5 to 1, was forced through the reactor surrounded by boiling water at such a rate that the contact time was 180 secs. The applied pressure was maintained at 60—80 atmospheres. Excess ammonia and water were removed. The isopropanolamines had the following composition:

% by weight

Monoisopropanolamine	37.5	
Diisopropanolamine	50.0	95
Triisopropanolamine	12.5	

EXAMPLE 11.

100 A mixture of a 60% solution (by weight) of ammonia in water and ethylene oxide in the ratio of seven mols. of ammonia to one of ethylene oxide, was continuously fed to the reactor under a pressure of 68—80 atmospheres. The reactor was surrounded by a bath of boiling water and the pumping rate adjusted to give a contact time of 126 secs. The conversion of ethylene oxide was complete. After the removal of excess ammonia and water, the product had the following composition:

% by weight 110

Monoethanolamine	50
Diethanolamine	33
Triethanolamine	17

EXAMPLE 12.

The experiment described in Example 11 was repeated with a bath temperature of 135° C. The anhydrous amines had the following composition:

	% by weight
Monoethanolamine	58
Diethanolamine	31
Triethanolamine	11

EXAMPLE 13.

An 80% by weight solution of ammonia in water was continuously reacted with ethylene oxide in a molar ratio of 8.5 to 1. The reactor was surrounded with a water bath boiling at 100° C. and the contact time adjusted to 200 secs. The applied pressure was 60—80 atmospheres. The finished product was found to contain 15% unreacted ethylene oxide.

The contact time was increased to 400 secs. and the product was then found to contain no unreacted ethylene oxide. After the removal of excess ammonia and water, the anhydrous amines obtained with the longer contact time had the following composition:

	% by weight
Monoethanolamine	59
Diethanolamine	29
Triethanolamine	12

EXAMPLE 14.

Example 13 was repeated with a bath temperature of 140° C. and a contact time of 120 secs. Reaction of the ethylene oxide was complete and the resulting amines had the following composition:

	% by weight
Monoethanolamine	72
Diethanolamine	22
Triethanolamine	6

EXAMPLE 15.

A mixture of a 95% by weight aqueous solution of ammonia and ethylene oxide containing ammonia and ethylene oxide in the molar ratio of 9 to 1, was continuously fed to the reactor which was surrounded by a bath boiling at 100° C. The pressure was 60—80 atmospheres and the contact time was 730 secs. It was found that only 30% of the ethylene oxide had reacted.

When the contact time was increased to 20 minutes it was found that the conversion of the ethylene oxide was complete. The anhydrous product obtained from the longer reaction consisted of:

	% by weight
Monoethanolamine	60
Diethanolamine	31
Triethanolamine	9

EXAMPLE 16.

Example 15, was repeated with the bath temperature raised to 149° C. and the contact time decreased to 92 secs. Conversion of the ethylene oxide was complete. The anhydrous product had the following composition:

	% by weight
Monoethanolamine	69
Diethanolamine	25
Triethanolamine	6

EXAMPLE 17.

A mixture of a 98% by weight solution of ammonia in water and ethylene oxide containing ammonia and ethylene oxide in the molar ratio of 9.6 to 1, was continuously fed to the reactor under a pressure of 60—80 atmospheres with a bath boiling at 100° C. surrounding the reactor. A contact time of 2 hours was necessary to obtain complete reaction of the ethylene oxide. The resulting ethanolamines contained:

	% by weight
Monoethanolamine	61
Diethanolamine	30
Triethanolamine	9

EXAMPLE 18.

A solution of ammonia in methanol containing 60% by weight of ammonia was mixed with ethylene oxide to give a mixture in which the molar ratio of ammonia to ethylene oxide was 7:1, and this mixture was passed through the reactor surrounded by a liquid boiling at 127° C. A pressure of 120—160 atmospheres was applied to the system and the contact time in the reactor was 120 seconds.

After the removal of excess ammonia and methanol the resulting amines contained:

	% by weight
Monoethanolamine	63
Diethanolamine	30
Triethanolamine	7

EXAMPLE 19.

A solution of ammonia in water and methanol containing 60% by weight of ammonia, 20% by weight of methanol and 20% by weight of water was mixed with ethylene oxide to give a mixture in which the molar ratio of ammonia to ethylene oxide was 7:1. The mixture was passed through the reactor surrounded by a liquid boiling at 109° C. A pressure of 120 to 160 atmospheres was applied to the system and the contact time was 120 seconds.

The resulting amines, after removal of the water, methanol and excess ammonia, had a composition similar to that of the amines obtained in Example 1.

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EXAMPLE 20.

5 A 50% solution by weight of ammonia in *n*-butanol was reacted with ethylene oxide in the reactor coil in a molar ratio of ammonia to ethylene oxide of 6.8:1. The reactor coil was immersed in a bath of liquid boiling at 127° C. and the pressure applied to the system was 120—160 atmospheres. A contact time of 132 seconds resulted in complete reaction of the ethylene oxide.

10 Excess ammonia and butanol were removed from the product and the resulting mixture of amines had a composition approximating closely to that of the amines obtained in Example 1.

EXAMPLE 21.

20 A mixture of ammonia and diethanolamine containing 95% by weight of ammonia was reacted with ethylene oxide in a molar ratio of ammonia to ethylene oxide of 10:1. The boiling bath temperature was 100° C., the applied pressure was 120—160 atmospheres and the contact time was 2 hours.

25 The resulting mixture of amines after removal of excess ammonia had the following composition:

	% by weight	
Monoethanolamine	51	
Diethanolamine	42	
Triethanolamine	7	30

EXAMPLE 22.

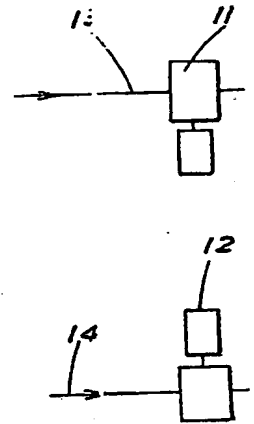
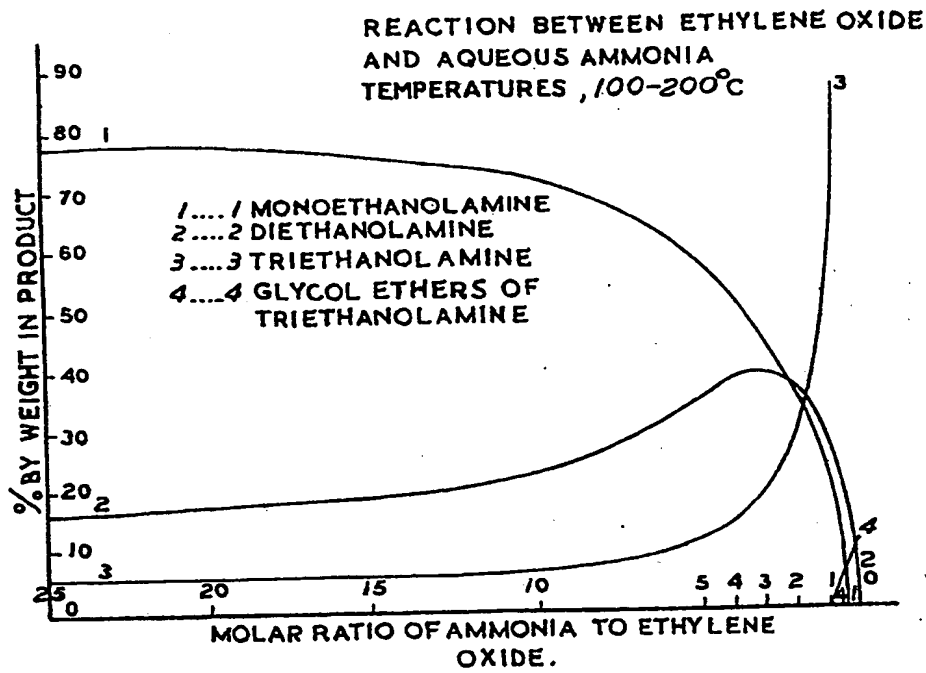
A mixture of ammonia and monoethanolamine containing 94% by weight of ammonia was reacted with ethylene oxide in a molar ratio of ammonia to ethylene oxide of 10:1. The boiling bath was maintained at 150° C., the applied pressure was 120—160 atmospheres and the contact time 5 minutes. The resulting mixture of amines, after the removal of unreacted ammonia, had the following composition:

	% by weight	
Monoethanolamine	69	
Diethanolamine	37	
Triethanolamine	4	45

REDDIE & GROSE,
6, Bream's Buildings, London, E.C.4,
Agents for the Applicants.

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FIG. 1.

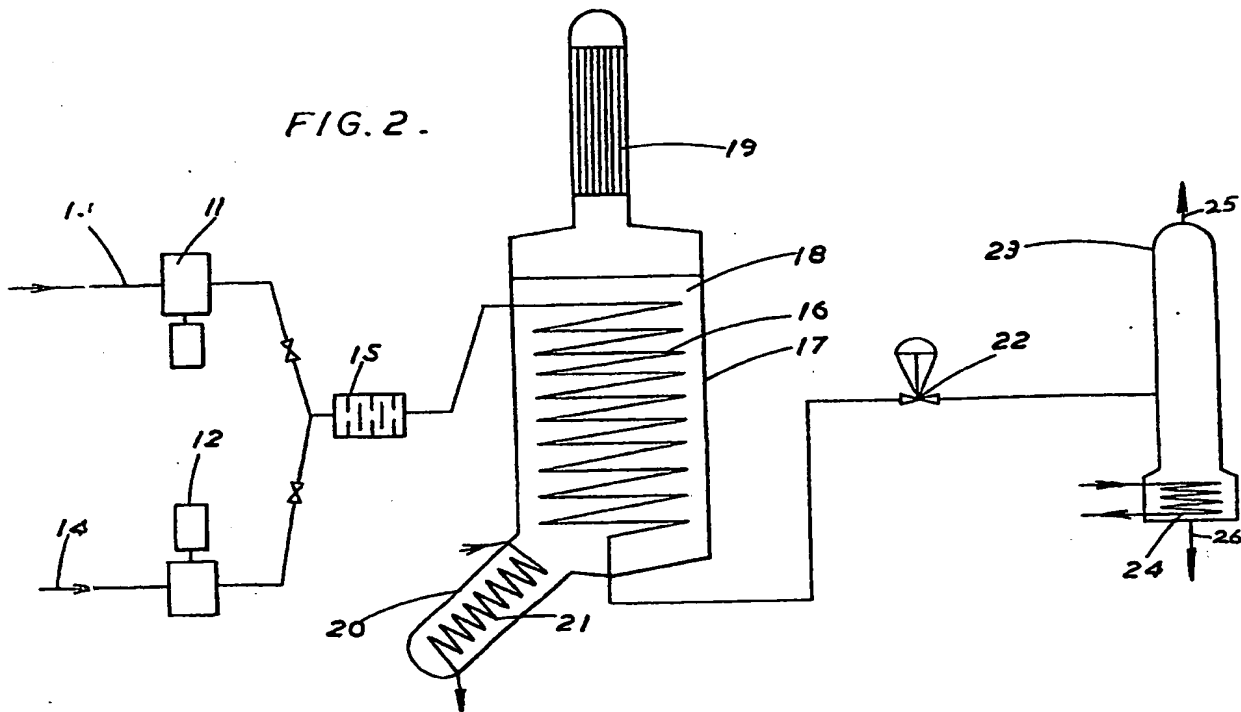


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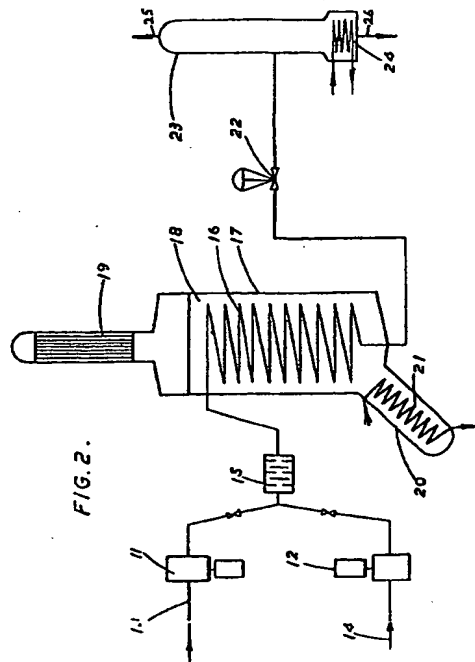
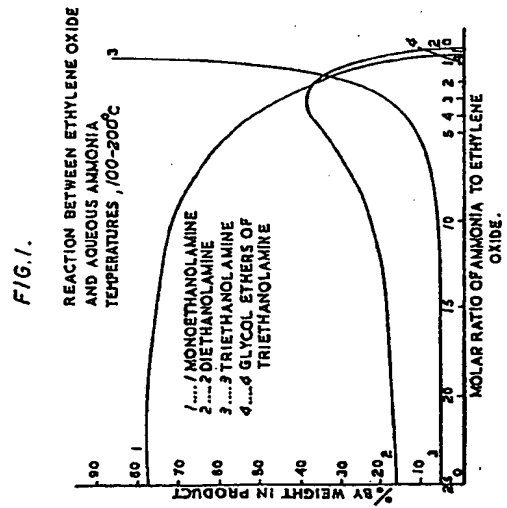
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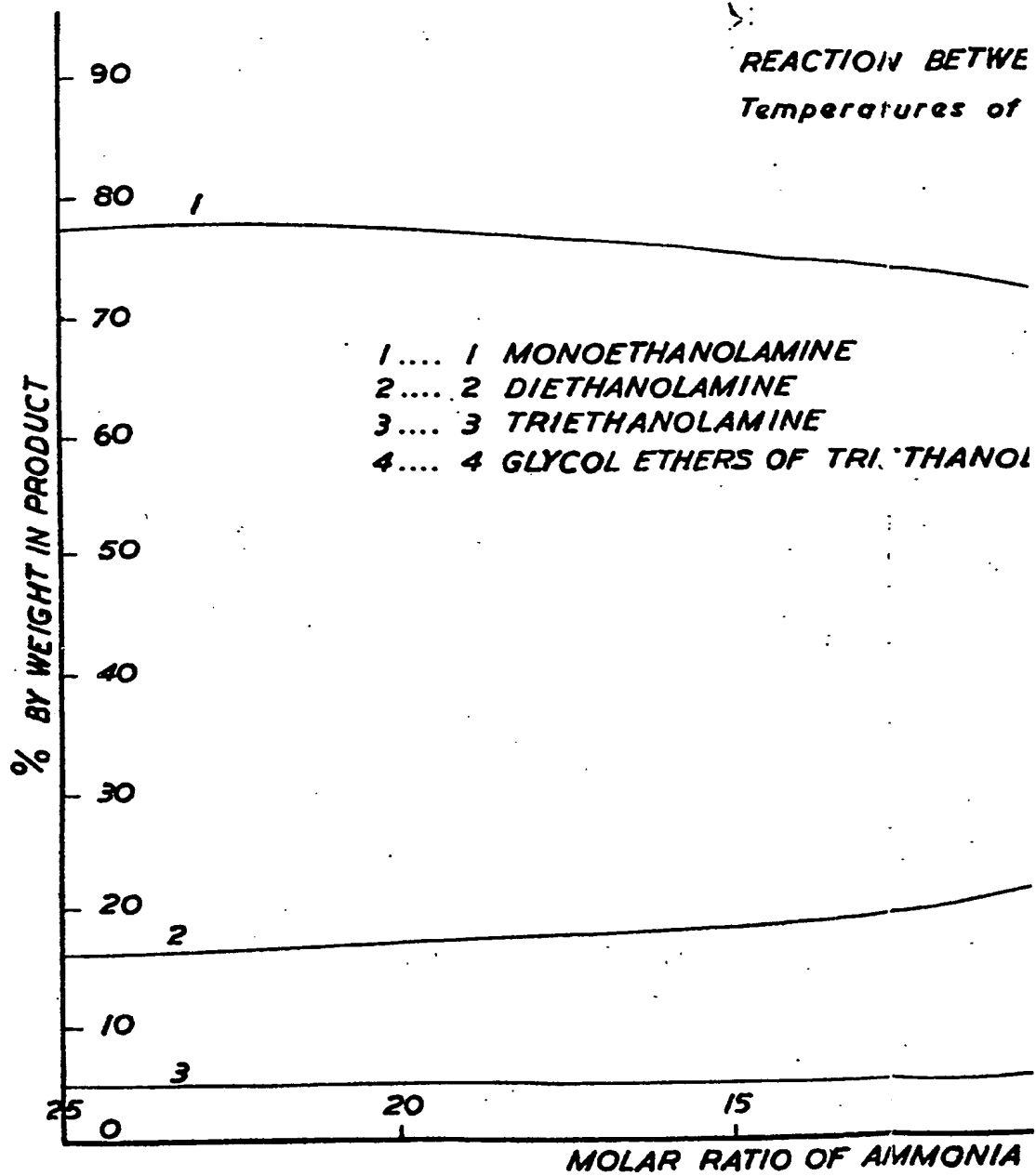
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FIG. 2.



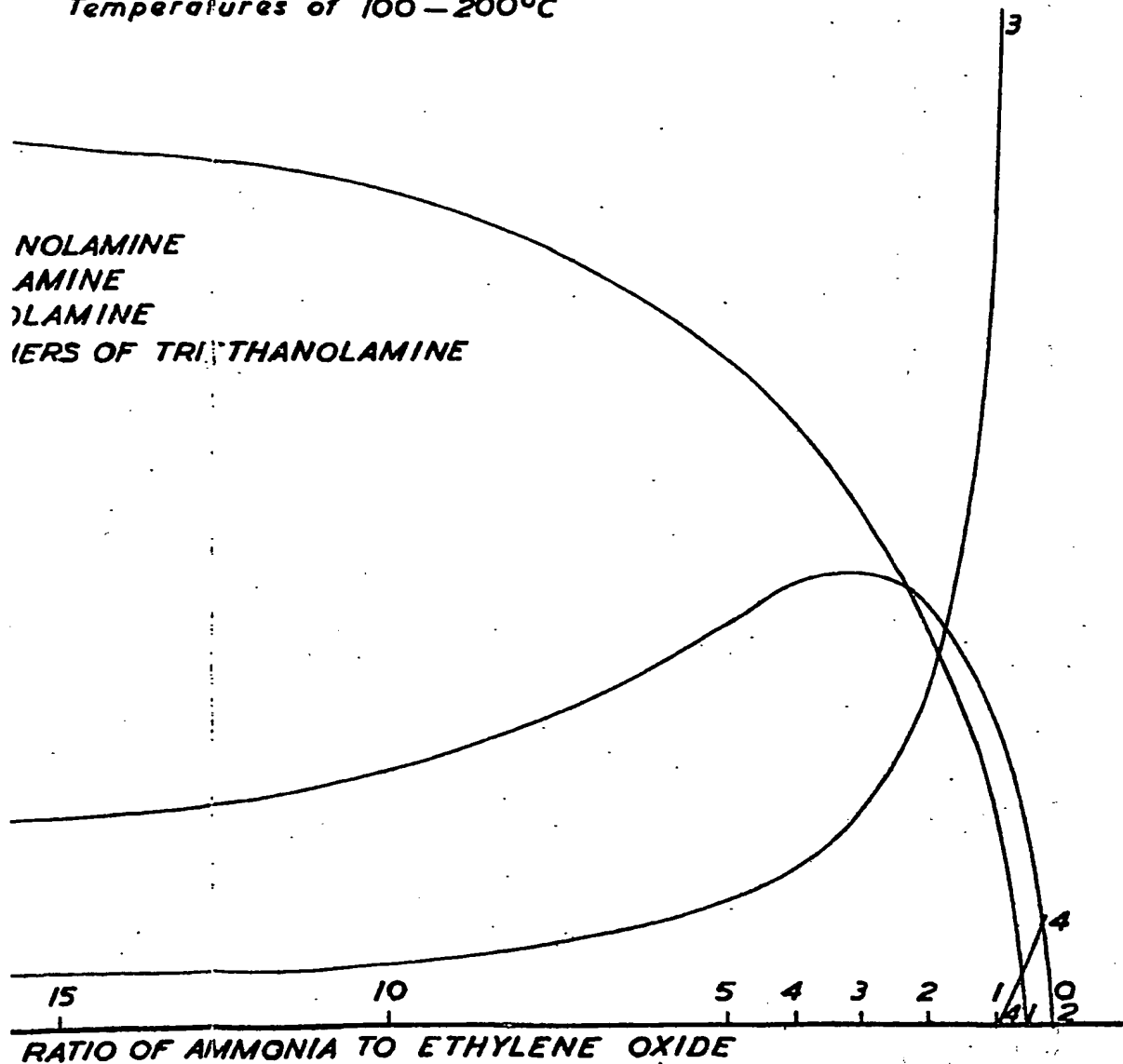
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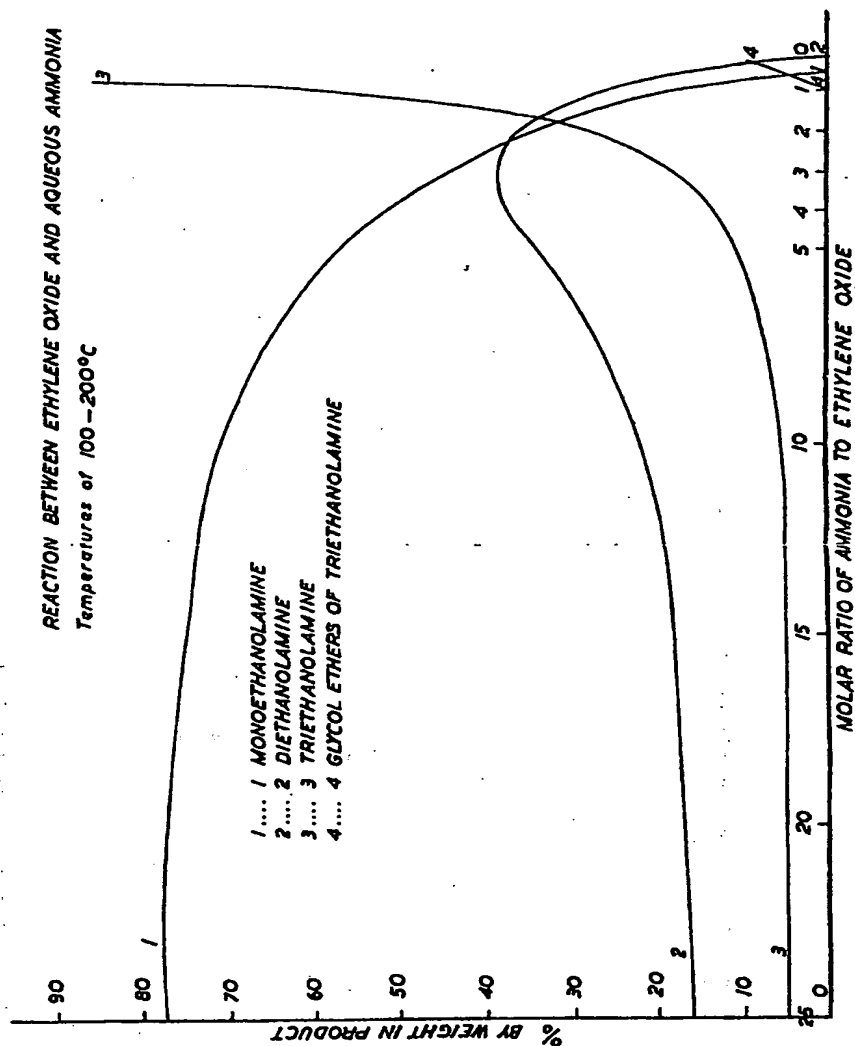


760215
1 SHEETPROVISIONAL SPECIFICATION
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REACTION BETWEEN ETHYLENE OXIDE AND AQUEOUS AMMONIA
Temperatures of 100 – 200°C



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